

## THE CLASSIFICATION OF CARBON COMPOUNDS.

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The system of classification adopted for a science at any given period registers quite accurately the state of the science at that period, and the changes in the classification therefore record its progress. It is, hence, practically impossible to give any intelligible description of the various methods of classification which have been employed for carbon compounds without at the same time sketching briefly the changing conceptions and theories of which they were to so large an extent the natural reflection, for without such a setting the picture would have no proper background or perspective.

The classifications which are considered are particularly those which have been used for textbook instruction in organic chemistry, and no place is given to those which have been devised solely for the patent offices, for reference, or for other special purposes.

Man being naturally of an inquiring mind, he has probably speculated upon the composition of this world of ours ever since he first appeared upon it, for in the oldest records we find theories concerning the elements of which it is composed.

The doctrine of the four so-called "elements"—earth, air, fire and water—was first enunciated in Greece by Empedocles, about 440 B. C., but generally bears the name of Aristotle. Neither Empedocles nor Aristotle regarded these elements as different forms of matter, but rather as different properties or manifestations of one original matter. Aristotle also added a fifth element, *οὐρα*, to which he ascribed an ethereal or immaterial character and which he assumed permeated the universe. As the oldest writings of India contain a similar theory of four elementary principles and an ethereal substance, it is possible that both Aristotle and Empedocles

were familiar with this fact and were only introducing into Greece this ancient Indian theory.

The oldest nations were familiar with the metals and refer to them frequently in their writings, but it should not be forgotten that some of the earliest chemical facts on record have to do with carbon compounds. The only acid known to the ancients was acetic (as vinegar), so that the name of this substance and the idea of acidity were expressed by closely related words; in the Greek, *ὄξος* for vinegar, and *ὀξύς* for acid; in the Latin, *acetus* and *acidus*. The first reagent of any kind mentioned was the extract of gall nuts, which Pliny says the ancients used to detect the presence of green vitriol in verdigris. The first salts artificially prepared were those obtained by the action of vinegar upon alkalies. The first crude attempts at distillation were with turpentine. The ancients were familiar also with fats, resins, organic coloring matters (like indigo and Tyrian purple), sugar, gums, the preparation of wine from grape juice, of beer from malted grain, of mead from honey, of soap from fats, and many other facts in these and related fields. Organic chemistry, therefore, does not give place in point of age to inorganic. Largely due to the influence of Alchemy, however, the object of which was the transmutation of baser metals into silver and gold, the mineral side of the subject was the first to be extensively developed.

According to the pseudo-Geber, all metals consisted of sulfur and mercury, in varying amounts and in different degrees of purity. The old Aristotelian "elements" he appears to have regarded as subsidiary constituents, or perhaps as the ultimate components of the sulfur and mercury. To the pseudo-Geber's two elements, Basil Valentine added a third, "salt," not meaning any particular compound but the properties characteristic of common sodium chloride, and he assumed these three to be the elementary constituents not only of metallic substances but of organic as well; sulfur endowing the substance with combustibility, or the property of changing in the fire, and also explaining color changes, mercury giving metallic properties and volatility, and salt representing the principle of solidification and of resistance to fire.

In spite of the great amount of experimental work carried out by the alchemists, and the large number of new facts discovered by them, their writings were so obscured by mysticism, exaggeration and deceit, that little real progress was made toward a more accurate understanding of the nature of chemical compounds which might be utilized in constructing a more satisfactory method of classification. No attempts were made to determine the actual constituents of compounds, for it was assumed that in the formation of a compound the original substances were annihilated and an entirely new substance created. Hence the only classification in vogue was a rough grouping of substances according to their physical properties, or apparent outward resemblance, and many of our common names are reminders of this bygone empirical method. Thus, olive oil and other vegetable and animal oils were grouped with oil of vitriol and oleum tartari (deliquesced potassium carbonate); spirit of wine (alcohol) with fuming spirit of Libavius (stannic chloride), spirit of hartshorn (ammonium hydroxide solution) and spirit of nitre (nitric acid); butter with butter of antimony (antimony trichloride) and other semi-solid metallic chlorides. Colorless solids, soluble in water and of characteristic well marked taste, were all classed as "salts," and this group thus included sugar.

The goal toward which the alchemists strove was the philosopher's stone, the grand elixir or the magisterium, as it was variously called, whose virtues were such that it could not only transmute baser metals into silver and gold, but could also prolong life indefinitely. As the claims concerning the transmutation of metals were increasingly discredited and the trickery and deception of the alchemists exposed, more investigators directed their attention toward the second great function of the philosopher's stone, the prolongation of life, and many compounds were discovered of considerable therapeutic value. Great interest was aroused by these investigations, and Paracelsus finally announced that "the object of chemistry is not to make gold but to prepare medicines." Thus, in the first half of the sixteenth century, chemistry began to develop in a new direction, at first not far removed from alchemy, but gradually diverging from it more and more widely, and approaching closer and closer

to medicine, until the coalescence of the two sciences appeared practically complete. And thus arose the period of iatro chemistry, when chemistry, which had long been looked upon as a valuable helpmeet to medicine, came to be regarded as the basis of the entire medical art.

Although in this period the chief development was again along the mineral side, probably because of the relatively greater simplicity and stability of these preparations, still no little organic investigation was conducted and a number of new compounds were added to the science. Little progress was made in gaining a truer insight into the character of chemical compounds, and hence no important changes in classification appear. Paracelsus himself, the founder of the iatro-chemical school, adopted Basil Valentine's three elements (sulfur, mercury and salt) as the basis of his doctrines.

By the middle of the seventeenth century, chemistry awakened to the fact that it had a destiny of its own to realize, struggled to its feet and, refusing longer to be supported by other sciences, started forward, to be sure rather unsteadily and uncertainly at first, but with the firm determination to do something for itself.

The history of chemistry proper begins with Robert Boyle about 1660, who taught that its main object was the determination of the composition of matter. Through his labors, and those of Rouelle and others, the terms "element" and "chemical compound" were more fully explained and appreciated; nevertheless many of their colleagues still adhered to the old alchemical or even the Aristotelian elements. Kopp, in his "*Geschichte der Chemie*," gives an excellent picture of the epoch-marking effect of Boyle's ideas:

"What a contrast is exhibited between the ancient idea of the cause of difference in various forms of matter and that which obtained at the time of Boyle! If we consider these two opposite conceptions historically, and the transition from the one to the other, they appear like two totally dissimilar pictures; but, like dissolving views, changing the one into the other by slow degrees. In the first place we have the Aristotelian idea, according to which, matter itself devoid of properties, becomes endowed with characteristic qualities by the addition of properties, and forms, when invested with these properties, the various substances known in nature; then this idea passes gradually into that of the alchemists, but becomes confused in the transition, inasmuch as the differences of physical condition and properties are no

longer regarded as the only causes of varieties in substances; the difference in chemical properties receives more attention, the existence of elements, the producers of such properties is assumed; and thus the path is prepared which leads to the idea of chemical composition. Then we see the Aristotelian theory gradually becoming indistinct, whilst the idea of the importance of the chemical department and composition of bodies assumes prominence, and at last we see clearly that the differences between the substances which nature presents to us in such overpowering numbers, or which we have ourselves formed artificially, depend upon differences in their chemical composition. The idea of chemical composition, which makes its first appearance indistinctly in the history of the chemistry of the Middle Ages, now forms the foundation of the science."

The most important and interesting problem at this time, and the one upon which most attention was focused, was the chemistry of combustion. Attempts to explain the phenomena of combustion finally led to the phlogiston theory of Stahl, which dominated the science from the end of the seventeenth through the eighteenth century.

In 1675, Nicolas Léméry published his "*Cours de Chimie*," which soon became one of the most popular textbooks of the time and passed through thirteen editions during its author's lifetime. In it he divided all natural substances into mineral, vegetable, and animal; including in the second group plants, resins, gums, fungi, fruits, acids, juices, flowers, mosses, manna and honey; and under the third heading describing the various parts of animal bodies. This classification was quite generally adopted, and thus arose a distinct separation of mineral chemistry from the chemistry of substances occurring in plants and animals. The phlogistonists had previously opposed any such subdivision, contending that the differences observed depended upon a variation in the composition of the bodies classed under the three heads. So Becher, in 1669, argued that the same elements occur in the three natural kingdoms, but that they are combined in a simpler manner in mineral substances than in vegetable or animal. Stahl, in 1702, asserted that in vegetable as well as in animal substances the watery and combustible principles predominated, and that these ultimate constituents made their appearance when the organic compound was heated out of contact with air, water and combustible charcoal being



formed. These ideas were successfully combated by Boyle, who had shown, as early as 1661, in his "Sceptical Chymist," that the application of heat leads to quite different results depending upon whether air is present or not, and that the various residues thus obtained are unlike.

Many organic substances were discovered during this phlogiston period, but their real composition (even qualitative) remained unrecognized. For example, it was assumed that the ultimate constituents of alcohol were oil and water, or a combustible and a mercurial principle. By far the greater number of the investigations recorded were still in the inorganic field, probably for reasons already given, and also because it had not as yet been possible to prepare organic compounds synthetically. While, as has been said, many authors adopted Léméry's method of separating mineral, vegetable and animal substances, others still adhered to the old system of grouping together all acids (sulfuric with lactic, tartaric, etc.), all salts, etc.

Boyle's influence was soon effective in directing a closer scrutiny of the composition of compounds, and gradually the true elements were isolated and studied.

The discovery of the composition of carbonic acid gas by Lavoisier in 1775, and that of water by Cavendish, showed the presence of carbon and hydrogen in alcohol (1784). Lavoisier, having established the true principle upon which combustion depends, analyzed various organic substances and came to the conclusion that vegetable substances were composed generally of carbon, hydrogen and oxygen, while animal substances contained also nitrogen and occasionally phosphorus. He did not distinguish organic chemistry as a special branch of the science, or define it as "the chemistry of the compound radicals." He discussed all acids together, subdividing them into mineral, vegetable and animal.

Macquer, who was professor of medicine in the University of Paris, and a contemporary of Lavoisier, in his "Elements of the Theory and Practise of Chymistry" (English translation of 1775) discusses mineral, vegetable and animal oils together, and in the separate sections of his work devoted to vegetable and animal

chemistry divides the subject according to the method of treatment employed to obtain the substance rather than according to the character of the substance itself. Thus we have as the main headings, "Operations on unfermented vegetables," "Operations on fermented vegetable substances," and "Operations on animal substances."

Fourcroy (about 1790), however, in his well-known text-book, makes a clean-cut division, placing the vegetable acids in the section dealing with the vegetable kingdom, and the animal products all under the animal kingdom.

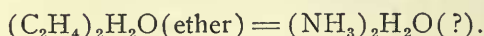
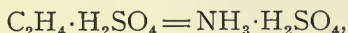
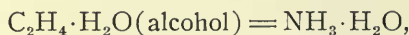
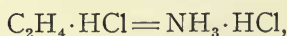
It should be noted that at this time carbon was supposed to exist as such in plants and animals. So Chaptal, in 1791, says:

"Carbone exists ready formed in vegetables. It may be cleared of all the volatile and oily principles by distillation, and, by subsequent washing in pure water, it may be deprived of all the salts which are mixed and confounded with it."

In Thomson's "System of Chemistry" (third edition, 1807), marsh gas and olefiant gas are discussed with the element carbon, but the other carbon compounds are scattered under various headings where they are mixed in with inorganic substances.

In the text-books and treatises on chemistry at this period it was customary to combine mineralogy and geology with the mineral part, botany with the vegetable section, and physiology with the portion dealing with animal chemistry, while occasionally physics received as much space as chemistry in the introductory chapters.

The ætherin theory of Dumas and Boullay, propounded by them in 1815, and later adopted by Berzelius, was an adaptation of the early theories concerning the composition of organic compounds (by which they were supposed to consist of an aqueous and a combustible principle) to new conditions. In their theory, many derivatives of alcohol were regarded as compounds of  $C_2H_4$  (to which Berzelius had given the name "ætherin"), in the same way that ammonium salts are derived from  $NH_3$ :



The attempt was made to apply this system of classification to other derivatives of alcohol and even to extend it to all organic compounds; but it never won any widespread recognition.

Berzelius, in 1817, explained the difference between inorganic and organic compounds by stating that every oxidized inorganic compound contained a simple radical, while organic compounds consisted of oxides of compound radicals; and that in vegetable substances the radical usually consisted of carbon and hydrogen, while in animal substances it consisted of carbon, hydrogen and nitrogen. He therefore defined organic chemistry as "the chemistry of the compound radicals" (1843). His conception of the structure of organic compounds was a dualistic electro-chemical one, in which the organic radicals played the same rôle as the elements in inorganic compounds; thus, both electro-positive and electro-negative radicals were assumed.

Gmelin, in the first edition of his great "Handbook" (1817), says that a clear distinction should be made between inorganic and organic chemistry, but that this is a distinction which can be more readily felt than strictly defined. He describes inorganic compounds as binary compounds, the simplest consisting of compounds of two elements, a basic oxide or an acid oxide, which can again unite to form a binary compound of a higher order, *i. e.*, a salt. Organic substances, on the other hand, are at least ternary compounds, or are composed of three simple substances, generally united in less simple ratio than in inorganic. Hence, he includes in the inorganic portion of his book methane, ethylene, cyanogen, and the like. He adds, further, that organic compounds cannot, like the inorganic, be artificially built up from their elements.

Berzelius also supported the last statement, claiming that in living structures the elements obeyed totally different laws from those which regulate their behavior in the inanimate world. Organic bodies were thus regarded as the special products of a mysterious vital force and, although he admitted that bodies occurring in nature might be converted into other organic compounds by chemical reactions, he maintained that none could ever be built up from their elements. Consequently, Wöhler's production of urea from am-



monium cyanate in 1827, being an incomplete synthesis, did not immediately overthrow the vitalistic doctrine. Then too, this synthesis remained for some time the only case of the kind, and urea itself was regarded as standing halfway between inorganic and organic compounds, because of the ease with which it decomposed into carbon dioxide and ammonia.

As the result of the classic researches of Liebig and Wöhler, in 1832, upon the radical of benzoic acid, the radical theory was enlarged by both Berzelius and Liebig.

Dumas, in 1837, explained the origin of so large a number of organic compounds from so small a number of elements, by stating that the latter unite to various radicals, which occasionally act as chlorine or oxygen, and occasionally as a metal. Cyanogen, ethyl, benzoyl, etc., were therefore said to constitute the elementary bodies of organic chemistry, their elementary components only being recognized when the organic nature of the compound was entirely destroyed. It is easy to see therefore why the search for these organic radicals was vested with such interest. In fact, the discovery and isolation of these radicals became the most interesting problem of the day and led to many valuable results.

In the text-books of this date, we find practically all organic compounds grouped under the two headings of Vegetable and Animal Chemistry; very few organic substances remained in the Inorganic part. An ever increasing number of these compounds found place in the separate chapters on Carbon and its Derivatives. Thus, in the manual compiled by Webster in 1826, when lecturer in chemistry at Harvard University, we find, in addition to CO, CO<sub>2</sub>, and other simple compounds previously discussed with carbon, also the chlorides of carbon, cyanogen, cyanogen halides, HCN, thiocyanic acid, CS<sub>2</sub> and thiocarbonates; in Dumas' great "*Traité de Chimie*" (1828) also rose oil, naphthalene, sweet oil of wine, naphtha, petroleum, turpentine, cyanic and fulminic acids. In most cases, the acids, being most important, were the first to be considered under the heading Vegetable Chemistry, then followed the other groups—oils (fatty and volatile), carbohydrates, camphors, alkaloids, etc., the rapid increase in the knowledge of organic compounds being

exhibited in the closer and more logical classification within the groups. The term "organic chemistry," to include both vegetable and animal chemistry, used by Berzelius in his "Handbook," was quite generally adopted.

In 1836, Laurent advanced his nucleus theory which, although never generally accepted, was used by Gmelin in his "Handbook," with certain alterations, as a foundation for a classification of organic compounds. According to this theory, every organic compound contains a group of atoms termed a "nucleus" or "germ." Primary nuclei consist of carbon and hydrogen, and in these the hydrogen may be replaced by other elements or groups of elements, thus giving rise to derived or secondary nuclei, analogous in composition and chemical properties to the primary nuclei. Other atoms may be attached to this nucleus, or they may quite surround it, and when these are removed the primary nucleus reappears.

In 1839, Dumas developed his substitution theory to a theory of chemical types. An advance was made in the replacement of the dualistic formulas by unitary ones.

Gerhardt's residue theory appeared at about this time. It may well be explained in comparison with the older radical theory. According to the latter, ethyl nitrate, for example, was regarded as the nitrate of ethyl oxide,  $(C_2H_5)_2O \cdot N_2O_5$ ; while, according to Gerhardt, the combination of the nitric acid and alcohol occurs in such a manner that one compound gives up a hydrogen and the other a hydroxyl, forming water, the two "residues" then uniting to ethyl nitrate.

The discovery of the compound ammonias by Wurtz (1849) and Hofmann led to the arrangement of organic compounds on types of various simple inorganic bodies. For example, it was assumed that the hydrogen in ammonia not only could be replaced atom for atom by other elements, but also by compound radicals.

Gerhardt's type theory was really a combination of his residue theory with the older radical theory. His four fundamental types were hydrogen, hydrochloric acid, water and ammonia;  $H-H$ ,

$H-Cl$ ,  $H-O-H$ ,  $N \begin{array}{c} \diagup H \\ -H \\ \diagdown H \end{array}$ , to which Kekulé subsequently added

methane,  $\text{CH}_4$ . These proving insufficient, multiple and mixed types were invented.

So early as 1838, Gerhardt had called attention to the fact that by the action of sulfuric acid upon various substances compounds were produced in which the characteristic properties of the constituents were not present. To distinguish such, he coined the term "copulated compounds." His original views were considerably enlarged and modified by Berzelius. According to this point of view, many radicals were assumed to be composed of several simpler ones. Thus, the fact that many monobasic acids (written on the water type) could frequently be decomposed with liberation of the CO group as  $\text{CO}_2$ , together with the alcohol radical, caused the acid radicals to be looked upon as made up of CO and an alcohol radical,  $\text{CH}_3 \cdot \text{CO} \text{---} \text{O} \text{---} \text{H}$ , instead of  $\text{C}_2\text{H}_3\text{O} \text{---} \text{O} \text{---} \text{H}$ , and paved the way for the modern structural formulas.

It was Williamson who showed that the existence of compound radicals could be assumed just as well for inorganic as for organic compounds, and that organic chemistry could no longer be correctly designated as "the chemistry of the compound radicals."

With the discovery of substances common to both plants and animals, the subdivision of organic chemistry into vegetable and animal chemistry was quite generally abandoned.

Gmelin says in his "Handbook" (Vol. VII., pp. 4 and 5):

"Carbon is the only element which is essential to organic compounds; every one of the other elements may be absent from particular compounds, but no compound which in all its relations deserves the name "organic" is destitute of carbon. . . . If we were to regard as organic those carbon compounds which have been classed hitherto among inorganic substances, namely carbonic oxide, carbonic acid, sulfide of carbon, phosgene, cast iron, etc., we might define organic compounds simply as 'the compounds of carbon'; but organic compounds are still further distinguished by containing more than one atom of carbon. . . . Hence the term 'organic compounds' includes all primary compounds containing more than one atom of carbon."

This last qualification was unfortunate, for it was soon shown that the atomic weight of carbon was 12, instead of 6, and that, therefore, methyl alcohol and formic acid contained only one atom of carbon and would be excluded from organic compounds by the above definition.

Kane, several years before (about 1840), had exposed himself to no such difficulty. In his "Elements of Chemistry" he discussed all organic compounds as carbon derivatives and prefaced this chapter with the following remarks:

"The element which is peculiarly organic and which, with the one exception of ammonia, exists in all bodies derived from an animal or vegetable source, is carbon. It is hence that I have deferred the description of carbon and its compounds until I could pass directly from it to the great variety of organic bodies of which it is the basis. With the constituents of inorganic bodies it has but an accidental connection; for, as I shall hereafter show, there is no form of carbon which has not at some time made part of an organized being."

In the great "Handwörterbuch" of Liebig, Poggendorff and Wöhler (1851), we find the following:

"Since, however, a natural boundary between organic and inorganic compounds in general does not exist, and can no longer be assumed, since we know that both are subject to the same combining laws, and since, therefore, if a separation is desired, an artificial and arbitrary boundary line must be drawn, it appears simplest to designate organic chemistry directly as 'the chemistry of the carbon compounds,' and only a few, namely the simplest carbon compounds— $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{COCl}_2$ ,  $\text{CS}_2$  and carbamic acid—are more conveniently referred to inorganic chemistry."

Kekulé later (1866) expressed himself in similar vein. He says:

"We must come to the conclusion that the chemical compounds of the vegetable and animal kingdoms contain the same elements as those of inanimate nature. We know that in both cases the same laws of combination hold good, and hence that no differences exist between organic and inorganic compounds either in their component materials, in the forces which hold these materials together, or in the number or mode of grouping of their atoms. . . . If, however, for the sake of perspicuity, a line of demarcation is to be drawn, we must remember that this boundary is an empirical rather than a natural one and may be traced at any point which seems most desirable. If we wish to express by 'organic chemistry' that which is usually considered under the name, we shall do best to include all carbon compounds. We, therefore, define organic chemistry as 'the chemistry of the carbon compounds,' and we do not set up any opposition between inorganic and organic bodies. That to which the old name of organic chemistry has been given, and which we express by the more distinctive term of the chemistry of the carbon compounds, is merely a special portion of pure chemistry, considered apart from the other portion only because the large number and the peculiar importance of the carbon compounds renders their special consideration necessary."

This change in the significance of the term "organic" chemistry



marks the passing of the old Vitalistic doctrine, and before we lose sight of it altogether, it may not be amiss to quote some interesting passages from Meldola's recent work on the "Chemical Synthesis of Vital Products." He says, among other things, that while it is quite true that we can produce in the laboratory substances identical with those formed in the living organism, in the majority of cases we cannot maintain that the syntheses are identical in their mechanism, and those who would "explain" the biochemical processes by a simple chemical equation should bear in mind the fact that "the sign connecting the two sides of the equation stands for the whole unexplored region of biochemical transmutations." We lack exact knowledge of the nature of the synthetic processes going on in the living organism, and there is little reason for believing that they have much analogy with our laboratory methods. In fact, we cannot duplicate in the laboratory the most fundamental of all these syntheses—the photosynthesis accomplished by plants, in which carbon dioxide is absorbed by an organic compound and the product decomposed with liberation of oxygen. While the author does not at all array himself on the side of the vitalists, he concludes, from the summary of experimental results recorded in his book,

"that the testimony of pure chemistry cannot, as it stands at present (*i. e.*, about 1904), be legitimately interpreted into a direct negation of Vitalism in any form. This negation may, and probably will be made possible in the future, when our chemical methods have been made to approximate more closely to the vital methods."

Until about the year 1830, it was supposed that the same element could present itself in only one form, endowed with one invariable set of properties, and that from the combination of the same elements in the same proportions, only one and the same substance could possibly result. The discovery of isomeric compounds, consequently, led to a more careful search for the cause of the difference in the properties of substances with the same percentage composition. With the establishment of the correct relations of atom, molecule and equivalent, the way was opened for the valence hypothesis, and in 1858 Kekulé said:

"I do not regard it as the chief aim of our time to detect atomic groups which, owing to certain properties, may be considered radicals, and thus to



include the compounds under certain types, which in this way have scarcely any other significance than that of type or example formulas. I am rather of the opinion that the generalization should be extended to the constitution of the radicals themselves, to the determination of the relation of the elements among themselves, and thus to deduce from the nature of the elements both the nature of the radicals and that of their compounds."

The recognition of the quadrivalence of carbon atoms and their power of uniting with each other, accounted for the existence and combining value of radicals, as well as for their constitution. The type theory therefore found a broader generalization and amplification in the extension of the valence hypothesis of Kekulé and Couper to the derivatives of carbon.

While in years gone by, as has been said, the classification of carbon compounds was mainly or exclusively according to the source from which they were obtained, in modern times the classification has been based solely upon their structural relations and entirely independent of their origin.

One of the first to adopt this method of classification was Löwig, in 1840. Gmelin, in 1848, arranged carbon compounds in his "Handbook" according to the number of carbon atoms they contained, and subdivided them on lines similar to those suggested in Laurent's nucleus theory, as already mentioned.

Schiel, in 1842, remarked upon the fact that alcohol radicals form a simple and regularly graded series of bodies, of which the properties as well as the composition exhibit corresponding regular gradations, and he predicted the existence of other similar series. Shortly afterward, Dumas pointed out that the fatty acids constitute such a series. Gerhardt, in his "*Précis de Chimie Organique*" (1844), collected a large number of such groups, gave to them the name "homologous series," and distributed them under the general divisions suggested by his type theory. This recognition of homologous series as the units in classifying organic compounds was a great step in advance, simplified the classification enormously, and was very fruitful in stimulating investigation to discover other similar series.

The terms "fatty" and "aromatic" chemistry appeared about 1858. At first used in more restricted sense, they were gradually

extended until the former covered all acyclic compounds and the latter nearly all cyclic. This subdivision of organic chemistry has been generally adopted (with few exceptions) ever since. More recently, it has been found advisable, particularly in the larger textbooks, to split up aromatic chemistry into carbocyclic and heterocyclic. So that we now have the three classes, fatty (or aliphatic), carbocyclic (or isocarbocyclic), and heterocyclic. And yet this classification is no longer satisfactory, for there is no sharp dividing line between straight-chain and cyclic compounds, the one merging gradually into the other. Certain cyclic structures (as the ethylene oxides, lactones, lactames, imides, etc.) are invariably discussed under fatty chemistry, and certain straight-chain compounds (like the olefin terpenes and their derivatives) are generally taken up under aromatic chemistry, while the alicyclic compounds, as their name indicates, form the natural transition from aliphatic to cyclic structures.

With the filling in of the gaps heretofore existing between aliphatic and aromatic chemistry, the time seems appropriate for a change in our classification of carbon compounds which shall recognize the essential unity of the subject, and no longer give the impression that organic chemistry is composed of three varieties of chemistry—fatty, carbocyclic and heterocyclic.

The method which appeals particularly to the writer, and which he has followed with his classes at Columbia University for the past ten years, is to begin with the hydrocarbons, as the simplest carbon compounds, and discuss in succession the various series of hydrocarbons, saturated and unsaturated, acyclic and cyclic, before passing on to the next group. After a careful consideration of these fundamentally important compounds, other classes of carbon compounds are taken up in similar manner; all of the simple halogen derivatives being considered together, all the nitro bodies, all the alcohols, and so on. All other classes are very conveniently regarded as derivatives of the hydrocarbons. With a knowledge of the properties of the various series of hydrocarbons, the study of their derivatives then resolves itself chiefly into the following questions: (1) What are the characteristic properties of the group under con-

sideration (be it halogen, amino, carboxyl, or any other group)? (2) In what manner are its properties influenced by the hydrocarbon nucleus to which it is attached, and by the other groups present? (3) How are the properties of the entire molecule likely to be affected by the introduction of such an element or group? To take a single case, by way of illustration, the simple hydroxyl derivatives of the hydrocarbons are numerous and important, and certain well defined characteristics cling to the hydroxyl group irrespective of the particular hydrocarbon nucleus to which it is attached. Thus, its hydrogen may be replaced by metals (giving alcoholates or phenolates), by hydrocarbon radicles (giving ethers), by acid radicals (giving esters), or the entire hydroxyl may be replaced by a halogen by acting upon it with a phosphorus halide. That the behavior of this hydroxyl group is influenced, however, by the hydrocarbon nucleus to which it is attached, can be seen at once by comparing a phenol with an alcohol. Further, the presence of the hydroxyl group alters the properties of the entire molecule, as appears immediately when we compare the behavior of benzene and of phenol towards bromine, nitric acid, oxidizing agents, and so forth.

In this way, the characteristic properties of the different substituents may be firmly fixed in the mind, as well as the general nature of the various classes of organic compounds, and the student learns to associate certain chemical reactions with certain chemical structures, and to reason intelligently from a given structural formula as to the chemical behavior of the substance, whether he ever heard of the compound before or not, thus learning not only to deduce correct constitutional formulas, but also to grasp at a glance the chemical properties summarized by such formulas.

This method of classification saves an immense amount of repetition and brings home very clearly the fundamental properties and relationships of organic compounds, as well as the application of these properties in analytical and industrial chemistry. Another advantage which follows from this arrangement, is the manner in which it lends itself to laboratory illustration. As all compounds containing the same substituting element or group are

discussed together, examples for laboratory practice may be drawn from either the acyclic or the cyclic field.

The author claims no originality for this suggested classification, except so far as certain details are concerned, for it was recommended and adopted so long ago as 1864 by that distinguished Russian chemist, Butlerow, in his "Lehrbuch der organischen Chemie," and has won adherents in this country in Professors W. A. Noyes, Kremers, and possibly others. My reasons for presenting it at the present time are the evident need for some change in our present system, brought into the foreground by the approaching publication of the new edition of Beilstein's monumental "Handbuch der organischen Chemie" and the creation of national commissions on the nomenclature of organic compounds, and my firm belief, as the result of experience, that the adoption of such a system will aid in inspiring and stimulating greater interest in the study of organic chemistry.

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